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Fate of Noble Metals during the Pyroprocessing of Spent Nuclear Fuel

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Abstract – During the pyroprocessing of spent nuclear fuel by electrochemical techniques, fission products are separated as the fuel is oxidized at the anode and refined uranium is deposited at the cathode. Those fission products that are oxidized into the molten salt electrolyte are considered active metals while those that do not react are considered noble metals. The primary noble metals encountered during pyroprocessing are molybdenum, zirconium, ruthenium, rhodium, palladium, and technetium. Pyroprocessing of spent fuel to date has involved two distinctive electrorefiner designs that have resulted in significantly different noble metal removals. For one electrorefiner, the anode and cathode collector are horizontally displaced such that uranium is transported across the electrolyte medium. For this design, the noble metal removal from the uranium during refining is very high, typically in excess of 99.9%. For the other electrorefiner, the anode and cathode collector are vertically collocated to maximize uranium throughput. This arrangement has resulted in considerably less noble metal removal from the uranium, typically no better than 20%. An acceptable level of noble metal carry over is derived based on previous operating experience, current research, and fuel performance issues. A level of 50% carryover results in approximately 5 wt. % noble metals in the uranium product after ten pyroprocessing cycles. This amount of noble metals poses no potential problems to fuel fabrication efforts and reactor fuel performance.

I. INTRODUCTION

Uranium products are being recovered from Experimental Breeder Reactor-II (EBR-II) spent nuclear fuel by a pyroprocess at the Idaho National Laboratory (INL). The treatment process comprises a set of operations designed to recover uranium from radioactive fission products and place the fission products into acceptable waste forms.[1-2] The uranium products are currently being stored pending a disposition decision.[3] Treatment of the EBR-II spent fuel was initiated in June 1996 and continues currently on the balance of the spent fuels.

Batch operations performed on the spent fuel in the Fuel Conditioning Facility (FCF) include chopping, electrorefining, cathode processing, and casting. The FCF is an atmosphere-controlled, shielded hot cell facility where all operations are performed remotely by overhead cranes, electromechanical manipulators, or manual manipulators. Spent fuel is either dismantled into elements from assemblies or retrieved directly as elements from storage containers. Initial fuel element handling operations are performed in the air cell of FCF prior to their transfer to the argon cell for element chopping. Elements are chopped into segments by either a solenoid-driven or pneumatic press depending on the fuel type, driver or blanket, respectively. Driver fuel was utilized in the core region of the reactor and contains a highly enriched uranium-zirconium alloy where the zirconium content is 10 wt. %. Blanket fuel, consisting of depleted uranium, encircled the driver-core and contains considerably less fission products due to its lower enrichment.

Chopped fuel segments are loaded into an anode assembly which contains up to nine perforated baskets depending on the fuel type. The anode assembly is installed into the electrorefiner commensurate with the fuel type; Mark-IV for driver fuel and Mark-V for blanket fuel. Although the two electrorefiner vessels are identical in design, the electrode configurations, liquid contents, and process conditions are slightly different. During electrorefining[4] in both units, fuel is anodically dissolved in a LiCl-KCl eutectic salt such that the uranium transport and deposition as a recoverable cathode product is

feasible. In addition to the LiCl-KCl, other chloride species are present in the electrorefiner salt due to the oxidation of fission products, bond sodium, and actinides from the spent fuel. Those fission products that are oxidized into the molten salt electrolyte are considered active metals while those that do not react are considered noble metals. The noble metals encountered during pyroprocessing primarily consist of molybdenum, zirconium, ruthenium, rhodium, palladium, and technetium.

Cathode products, containing uranium and chloride salt, are processed in a vacuum distillation furnace (called the cathode processor) for the separation of salt from uranium. Distillation operations for the two electorefiner products are performed separately, but in the same cathode processor[5], to produce consolidated metal ingots. A casting step following distillation allows for isotopic dilution, if necessary, and sampling of the ingots for chemical analyses.

The context of this paper is to discuss and contrast the distribution of noble metals in the feed and products for the two fuel types and their associated electrorefining systems. This data may assist in the optimization of electrorefiner designs for commercial pyroprocessing applications. Finally, the effect of noble metal carryover on fuel fabrication and performance will be addressed in terms of thermal and radioactive properties of the fuel.

II. ELECTROREFINER SYSTEMS

As mentioned, two electrorefiner systems are currently in operation for the pyroprocessing of spent nuclear fuel at the INL. Briefly, the differences in the two systems, particularly the anode to cathode arrangements, will be given so that an understanding of the root causes of the distribution of noble metals is possible. Both electrorefiners are currently operated at approximately 500°C.

In the Mark-IV electrorefiner, the anode assembly includes four rectangular baskets, arranged in a cruciform geometry to dissolve uranium from the fuel segments. The cathode assembly consists of a solid-steel rod (mandrel) for deposition of uranium in the form of dendrites. Each electrode, anode or cathode, occupies one of four ports such that, electrorefining requires a minimum of two ports. The electrodes are both vertically and horizontally displaced such that uranium is transported vertically across the electrolyte medium and collected on the mandrel (Fig. 1). The approximate distance between the anode baskets and cathode mandrel is 50 cm. Below the molten salt electrolyte, a cadmium pool is present in the Mark-IV electrorefiner for recovery of dislodged dendritic material via a separate deposition operation.

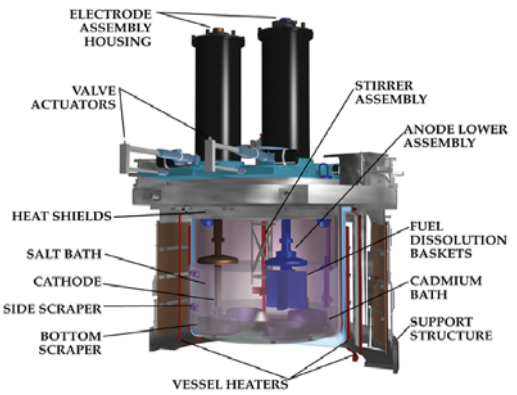

Fig. 1. Schematic of Mark-IV electrorefiner.

For the Mark-V electrorefiner, the anode and cathode are vertically collocated in a single module per port to maximize uranium throughput. The anode-cathode module (ACM) consists of nine curved baskets concentrically positioned in annular spaces between cathode cylinders (Fig. 2). The approximate distance between the anode baskets and cathode surface is 1 cm. During electrorefining, the baskets are rotated such that scrapers shear the uranium off the cathode cylinder surfaces and deposits fall into a product collector located below the ACM. The Mark-V electrorefiner does not require a cadmium pool due to the location of the product collector below the ACM.

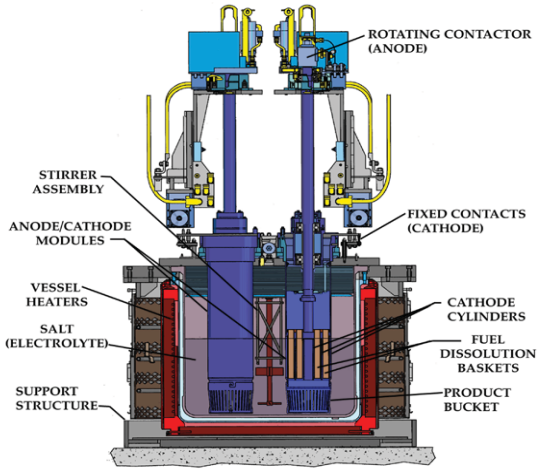

Fig. 2. Schematic of Mark-V electrorefiner.

Both the Mark-IV and Mark-V electrorefiners are operated using controlled current with an upper limit to the cell voltage. Since more uranium is processed in the Mark-V electrorefiner per anode and the cathode surface area is greater, larger applied currents are typically utilized than for the Mark-IV electrorefiner. A cathode stripping operation is also periodically employed during

the Mark-V operation to alleviate anode stalling caused by the buildup of cathode deposits.

III. NOBLE METAL DISTRIBUTION

A comparison of the primary noble metal fission products present in typical driver and blanket feed material is shown in Table I. All data are given in ppm relative to the feed uranium. Significantly more noble metals are associated with the driver fuel due to its higher enrichment as noted earlier. It also should be pointed out that the zirconium concentration in Table 1 for driver fuel is based on fission product zirconium and not on fuel matrix zirconium which is on the order of 10 wt. %.

TABLE I

Primary Noble Metals in EBR-II Driver and Blanket Feed

Fuel Type	Zr (ppm)	Mo (ppm)	Ru (ppm)	Tc (ppm)	Rh (ppm)	Pd (ppm)
Driver	10300	9300	4900	2200	1300	1100
Blanket	130	140	110	40	40	70

Following an electrorefining operation, noble metals may reside in three primary locations; two of which have been sampled. The uranium products and cladding hulls from the Mark IV and V electrorefiners are routinely analyzed for many different analytes including noble metals. The third location is the electrorefining vessels, which includes all of the hardware exposed to the electrolyte and the cadmium pool for the Mark-IV electrorefiner.

Although many scoping tests have been performed in the electrorefiners over a wide range of operating conditions, it is currently assumed that maximizing uranium recovery should be the primary goal of spent fuel processing.[6] Thus, early tests to retain zirconium (both from the driver fuel matrix and fission product) in the cladding hulls are not considered the current reference position. The consequence of this position is that zirconium will either be codeposited in the uranium products, due to similar thermodynamic properties, or end up in the electrorefining vessels. As zirconium buildup occurs in the vessels, periodic removal operations may be necessary, particularly for the Mark-IV electrorefiner, to continue electrorefining.

An approximate distribution of noble metals in the three primary locations for both driver and blanket fuel types is shown in Table II. As stated, the values assume the reference position of maximizing uranium recovery, i.e. dissolving greater than 99% from the anode. For operations at both the Mark-IV and V electrorefiners, a maximum cutoff voltage of 0.7 V was assumed.[4] Since noble metals in the electrorefiner vessels are not quantified via routine sampling, the balance has been assumed to reside in the vessels.

TABLE II

Distribution of Noble Metals (wt. %) following Electrorefining of EBR-II Driver and Blanket Spent Fuel

Fuel Type	Uranium Products	Cladding Hulls	Electrorefiner Vessel
Driver	0.01	~75	~25
Blanket	~80	~15-20	~0-5

The disparity between the amounts of noble metals reporting to the uranium products is quite obvious for driver and blanket operations. The driver data is based on more than 10 years of processing and has been averaged for multiple batch operations. It has been postulated that the noble metal contamination of the driver uranium products is primarily due to suspended particles being trapped in the dendritic cathode structure based on their relative size.[6-7] Because of the trace amounts of noble metals in the blanket feed and their difficulty in detection, the data for blanket material is not quite as extensive as for the driver material and hence the approximate designation. For both values, Ru^{106} data has been used and assumed to be representative of all the noble metals.

The distribution of noble metals in driver cladding hulls has been published elsewhere[6]; whereas the data for blanket hulls is not as established and hence the uncertainty. Again, the trace amounts of noble metals in the blanket feed, and a limited hull sampling campaign, hinder their quantification.

Although the noble metals in the electrorefiner vessels are more difficult to quantify, there is indirect data to support either their presence or absence. For both the Mark-IV and V electrorefiners, the salt electrolyte is routinely analyzed and the noble metal content is below the detection capability of the analytical equipment. The cadmium pool in the Mark-IV electrorefiner is also routinely analyzed showing the presence of noble metals. Considering the fact that the solubility of noble metals in the cadmium pool of the Mark-IV electrorefiner was exceeded early in the program, the majority of the noble metals is most likely present in the cadmium as precipitates due to gravitational settling. Not to be ignored is evidence of adhering material to vessel surfaces. Corrosion coupons have been retrieved from the Mark-IV electrorefiner (both salt and cadmium regions) and indicated the presence of noble metals, which for the salt region is consistent with small particles adhering to dendritic uranium deposits.

As a matter of reference, an experiment was performed in the Mark-V electrorefiner utilizing 325 mesh screens in the anode baskets to reduce the noble metal content of uranium products. The typical opening

in the anode basket was reduced by approximately a factor of 100 with the 325 mesh screens. Results from the test indicated no effect on noble metal retention by the mesh screens, most likely due to the particle size of noble metal particulate.

IV. EFFECT OF NOBLE METAL CARRYOVER

Considering the wide behavior for noble metal carryover with respect to the current electrorefiner designs, the design of future electrorefining systems for commercial applications would appear to be well bracketed. A specification for noble metal carryover can therefore be derived based on the number of fuel processing cycles and fuel performance issues.

Shown in Fig. 3 are the steady-state levels of noble metal accumulation in the uranium products assuming multiple pyroprocessing cycles. The bases for the data are a U-10Zr alloy with enrichments similar to the EBR-II driver fuel but taken to 20 atom % burnup instead of the existing driver limit of 10%.[8] If an IFR ternary alloy fuel (U-20Pu-10Zr) is assumed to be the product of pyroprocessing[1], additional feedstock materials would drive the noble metal content to values less than those given in Fig. 3.

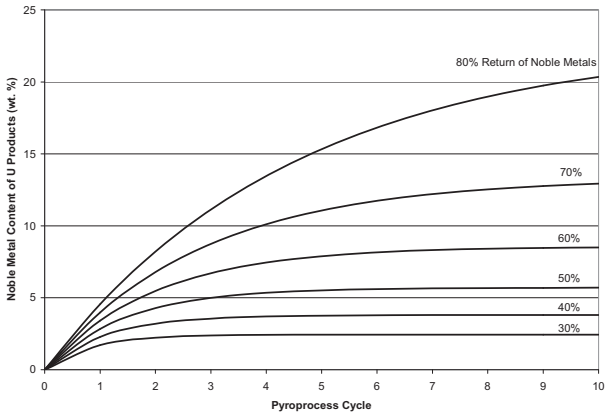

Fig. 3. Steady-state noble metal accumulation in uranium products.

For a Mark-V type electrorefiner system, an equilibrium value of greater than 20 wt. % would be expected for noble metals after ten processing cycles. At first glance, this would seem unacceptable in terms of fuel fabrication criteria and in fact, is confirmed by data from the original EBR-II melt refining process.[9] For that process, the noble metal or fissium content was limited to 5 wt. % based on the anticipated process capabilities. Assuming a noble metal carryover value of approximately 5 wt. %, at least 50% removal of the noble metals would be required from steady-state pyroprocessing operations.

Research with an electrorefining system specifically designed for noble metal removal has found that 75 wt. % removal is achievable under simulated conditions with surrogate materials.[10] Given the noble metal particle size for these tests (10 μm) and that typically found in spent metallic fuel (<10 μm)[7], a noble metal removal rate of less than 75% seems more likely with irradiated fuels. Thus, 50% noble metal removal emerges as a starting point for fuel evaluations.

In terms of fuel fabrication and performance, four characteristics are of interest with respect to noble metal content; alloy phase equilibria, thermal expansion and conductivity, and radioactivity. Again as a starting point, 50% noble metal removal or 5% carried over from multiple pyroprocessing cycles will be considered and incorporated into an IFR type ternary fuel. Direct substitution of noble metals, particularly molybdenum, for zirconium in the fuel matrix has a precedence given the history of metallic fuels.[11]

From a fabrication standpoint, 5 wt. % noble metals instead of zirconium will not have a significant effect on the alloy melting point or related casting temperature. For the uranium-fissium alloy, the casting temperature was 1400°C which included at least 150°C of superheat above the alloy's melting point.[12] A U-5Zr alloy has a melting point of approximately 1260°C.[13] From an in-reactor performance standpoint, it has been well established that alloying elements, such as molybdenum and zirconium, enhance the dimensional stability of uranium by maintaining the gamma phase over an extended range of operating temperatures.[11] Thus, displacement of zirconium by molybdenum and the other noble metals will not alter the gamma phase uranium alloys due to the mutual solubility of zirconium and molybdenum in uranium.

A key fuel characteristic during reactor operations is thermal expansion as it relates to fuel swelling which in turn causes cladding deformation or strain.[14] Shown in Fig. 4 are linear thermal expansion data versus temperature for several elements and alloys of uranium.[15] At a typical reactor fuel temperature of 727°C (1000K), the thermal expansion of the modified IFR ternary alloy falls between that of U-10Zr and the U-20Pu-10Zr ternary alloy. For all three primary noble metal elements, it is obvious how alloying lowers the thermal expansion of pure uranium.

Thermal conductivities are plotted in Fig. 5 at various temperatures for uranium and its alloys.[15-17] The thermal conductivity of a uranium alloy with 5 wt. % noble metals, in this case U-5Fs, is slightly higher than U-10Zr and significantly more than U-20Pu-10Zr. Since high thermal conductivity is a known attribute of metallic fuel, the addition of noble metals enhances conductivity beyond that of normal uranium alloys.

Considering the radioactivity of the noble metals, only ruthenium, specifically the isotope Ru^{106} with a half life of 365 days, may have an effect on fuel fabrication efforts. Since it's assumed that fuel fabrication operations would take place in a hot cell environment, the effect would be minimal and essentially non-existent after 5 years.

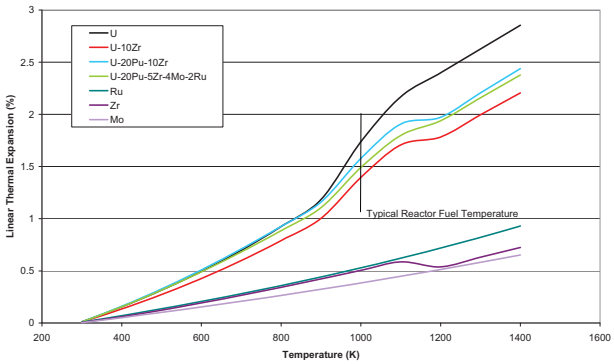

Fig. 4. Linear thermal expansion versus temperature for various elements and alloys of uranium.

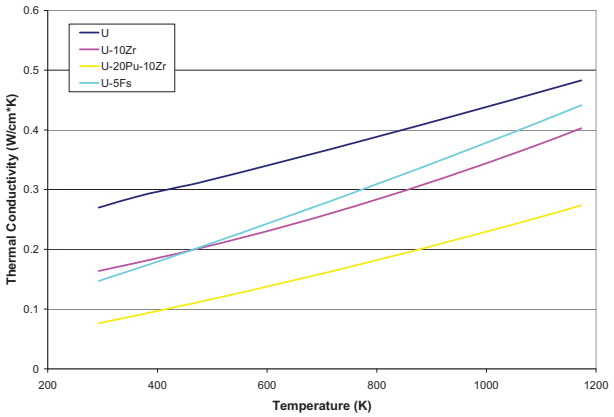

Fig. 5. Thermal conductivity versus temperature for various fuel materials

V. ELECTROREFINER DISCUSSION

Assuming the need to minimize noble metal carryover, a redesign of the current Mark-IV and Mark-V electrorefiners may be warranted based on previous electrorefiner designs.[18] Given in Fig. 6 are the anode to cathode layouts for the current electrorefiners as well as a redesigned electrorefiner where the anode resides below the cathode region. The anode is a basket-type container holding chopped fuel segments that is removed from the electrorefiner for cladding hull retrieval, similar to current anodes. Multiple mandrels act as cathodes which can be removed from the electrorefiner independently from the anode for harvesting. Several potential benefits are obvious for this design, namely: 1) removal of both anode and cathode for harvesting is not necessary providing a semi-continuous operation, 2) dendritic material that dislodges from the mandrel during electrorefining is recollected in the anode thus eliminating the need for a cadmium pool, 3) cathode product collection is performed out of the electrorefiner vessel as opposed to the more complex collection in situ, and most importantly 4) noble metal contamination of the uranium product is minimized due to gravitational effects.

VI. SUMMARY

The distribution of noble metals in the feed and products for blanket and driver fuel types was presented along with an explanation for the variability. The largest discrepancy occurs in the uranium products due to geometrical differences in the anode to cathode arrangement in the Mark IV and V electrorefiners. An acceptable level of noble metal carryover was derived based on previous operating experience, current research, and fuel performance issues. A level of 50% removal results in approximately 5 wt. % noble metals in the uranium product after ten pyroprocessing cycles. The thermal fuel properties of the ternary U-20Pu-10Zr alloy would not be significantly affected by displacing 5 wt. % of the zirconium with noble metals. Hence, future electrorefining systems for commercial applications should incorporate the condition of at least 50% noble metal removal as a design requirement.

Based on the findings of this paper, the effect of increased noble metal carryover on the overall pyroprocessing flowsheet should be considered. Several potential benefits standout for this scenario; 1) supplemental feed zirconium is not needed for fuel fabrication, 2) periodic zirconium removal campaigns from the electrorefiner are eliminated which simplifies the downstream processes, 3) noble metal clean out operations on the electrorefiner salt are minimized, 4) the need for the high level metal waste form is drastically reduced, and 5) technetium transmutation in reactor to resolve repository issues may be an option.

In addition, an electrorefiner system was proposed to minimize noble metal carryover based on existing technology. Several operational advantages were also given for the redesigned electrorefiner.

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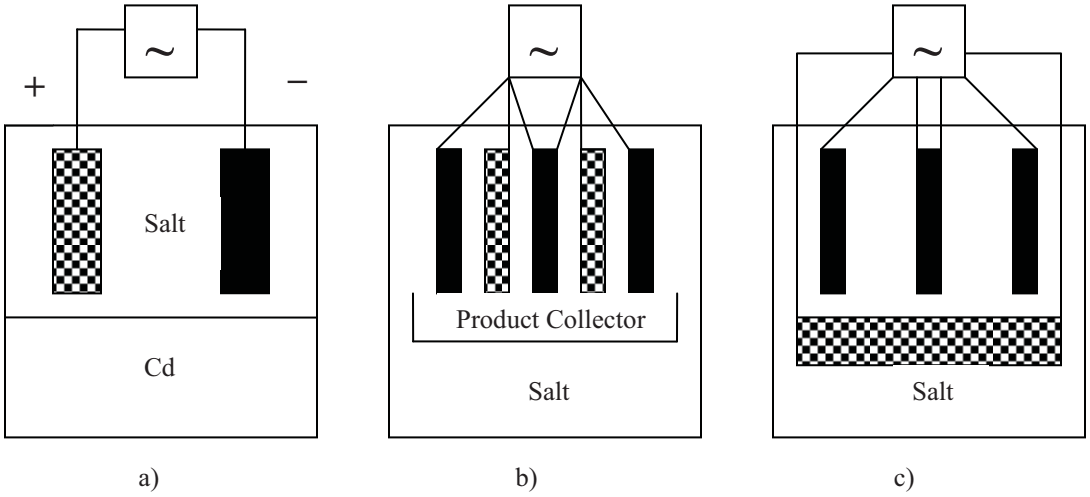

Fig. 6. Simplified anode and cathode layouts for a) Mark-IV electrorefiner, b) Mark-V electrorefiner, and c) new design electrorefiner

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